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FORM PTO-1390 (REV 12-29-99)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER ISTN-100	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 09/601888	
INTERNATIONAL APPLICATION NO. PCT/US99/02181		INTERNATIONAL FILING DATE 3 February 1999		PRIORITY DATE CLAIMED 9 February 1998	
TITLE OF INVENTION ION SEPARATION USING A SURFACE-TREATED XEROGEL					
APPLICANT(S) FOR DO/EO/US YANG, Arthur Jing-Min					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
<ol style="list-style-type: none"> 1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1). 4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. 5. <input type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> has been transmitted by the International Bureau. c. <input checked="" type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)). 7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ol style="list-style-type: none"> a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> have been transmitted by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). 9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). 10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). 					
Items 11. to 16. below concern document(s) or information included:					
<ol style="list-style-type: none"> 11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 12. <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 14. <input type="checkbox"/> A substitute specification. 15. <input type="checkbox"/> A change of power of attorney and/or address letter. 16. <input checked="" type="checkbox"/> Other items or information: Verified Small Entity Statement 					

U.S. APPLICATION NO. (if known, see CFR 1.53)

09/601888

INTERNATIONAL APPLICATION NO.
PCT/US99/02181ATTORNEY'S DOCKET NUMBER
ISTN-10017. ☐ The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):**Neither international preliminary examination fee (37 CFR 1.482)
nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO
and International Search Report not prepared by the EPO or JPO \$970.00International preliminary examination fee (37 CFR 1.482) not paid to
USPTO but International Search Report prepared by the EPO or JPO \$840.00International preliminary examination fee (37 CFR 1.482) not paid to USPTO but
international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$690.00International preliminary examination fee paid to USPTO (37 CFR 1.482)
but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$670.00International preliminary examination fee paid to USPTO (37 CFR 1.482)
and all claims satisfied provisions of PCT Article 33(1)-(4) \$96.00**ENTER APPROPRIATE BASIC FEE AMOUNT =****CALCULATIONS** PTO USE ONLY

\$ 670.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(e)).

\$

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
Total claims	51 - 20 =	31	X \$18.00
Independent claims	6 - 3 =	3	X \$78.00

\$ 558.00

\$ 234.00

MULTIPLE DEPENDENT CLAIM(S) (if applicable)

+ \$260.00

\$ 260.00

TOTAL OF ABOVE CALCULATIONS =

\$ 1,722.00

Reduction of 1/2 for filing by small entity, if applicable. A Small Entity Statement
must also be filed (Note 37 CFR 1.9, 1.27, 1.28)

\$ 861.00

SUBTOTAL =

\$ 861.00

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(f)).

\$

TOTAL NATIONAL FEE =

\$ 861.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property

\$

40.00

TOTAL FEES ENCLOSED =

\$ 901.00

Amount to be refunded:	\$
charged:	\$

a. ☒ A check in the amount of \$ 901.00 to cover the above fees is enclosed.b. ☐ Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees.
A duplicate copy of this sheet is enclosed.c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
overpayment to Deposit Account No. 19-1980. A duplicate copy of this sheet is enclosed.**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR
1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO

SHERMAN & SHALLOWAY
413 North Washington Street
Alexandria, Virginia 22314*Richard A. Steinberg*

SIGNATURE

Richard A. Steinberg

NAME

26,588

REGISTRATION NUMBER

Applicant or Patentee: Arthur Jing-min Yang Attorney's
Serial or Patent No.: \$371 of International PCT Application PCT/US99/02181 Docket No.: ISTN-100
Filed or Issued: Concurrently herewith
For: ION SEPARATION USING A SURFACE-TREATED XEROGEL

**VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY
STATUS (37 CFR 1.9(f) AND 1.27(c)) - SMALL BUSINESS CONCERN**

I hereby declare that I am

- ☐ the owner of the small business concern identified below:
☒ an official of the small business concern empowered to act on behalf of the concern identified below:

NAME OF CONCERN Industrial Science & Technology Network, Inc.
ADDRESS OF CONCERN CYBER Center, 1600 Pennsylvania Avenue, Suite 21, York, PA 17404

I hereby declare that the above-identified small business concern qualifies as a small business concern as defined in 13 CFR 121.12, and reproduced in 37 CFR 1.9(d), for purposes of paying reduced fees to the United States Patent and Trademark Office, in that the number of employees of the concern, including those of its affiliates, does not exceed 500 persons. For purposes of this statement, (1) the number of employees of the business concern is the average over the previous fiscal year of the concern of the persons employed on a full-time, part-time or temporary basis during each of the pay periods of the fiscal year, and (2) concerns are affiliates of each other when either, directly or indirectly, one concern controls or has the power to control the other, or a third party or parties controls or has the power to control both.

I hereby declare that rights under contract or law have been conveyed to and remain with the small business concern identified above with regard to the invention described in

- ☒ the specification filed herewith as identified above.
☐ the application identified above.
☐ the patent identified above.

If the rights held by the above identified small business concern are not exclusive, each individual, concern or organization having rights in the invention must file separate verified statements averring to their status as small entities, and no rights to the invention are held by any person, other than the inventor, who would not qualify as an independent inventor under 37 CFR 1.9(c) if that person made the invention, or by any concern which would not qualify as a small business concern under 37 CFR 1.9(d), or a nonprofit organization under 37 CFR 1.9(e). Separate verified statements are required from each named person, concern or organization having rights to the invention averring their status as small entities. (37 CFR 1.27)

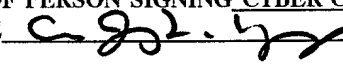
Each person, concern or organization having any rights in the invention is listed below:

NAME _____
ADDRESS _____
☐ INDIVIDUAL ☐ SMALL BUSINESS CONCERN ☐ NONPROFIT ORGANIZATION

NAME _____
ADDRESS _____
☐ INDIVIDUAL ☐ SMALL BUSINESS CONCERN ☐ NONPROFIT ORGANIZATION

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b))

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

NAME OF PERSON SIGNING Arthur Jing-min Yang
TITLE OF PERSON OTHER THAN OWNER President
ADDRESS OF PERSON SIGNING CYBER Center, 1600 Pennsylvania Avenue, Suite 21, York, PA 17404
SIGNATURE  DATE 7-20-2000

ISTN-100

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:

Arthur Jing-min YANG

Serial No.: Unassigned

Filed: Concurrently herewith

For: ION SEPARATION USING A SURFACE-TREATED XEROGEL

The Honorable Commissioner of
Patents and Trademarks
Washington, D.C. 20231

August 9, 2000

PRELIMINARY AMENDMENT

Sir:

Prior to the initial examination of the subject application, please amend the same as follows:

IN THE TITLE

Please amend the title to read --ION SEPARATION USING FUNCTIONALIZED GEL--.

IN THE SPECIFICATION

Page 1, lines 1-3, change "funded in part by a government grant from the Small Business Administration and the U.S. government retains certain rights to this invention" to --made with Government support under Contract No. DE-FG02-97ER82409 awarded by the Department of Energy. The Government has certain rights to this invention--.

Page 1, please delete lines 4-6 and insert the following new section:

--Cross-Reference To Related Application

This application is the National Phase entry, 35 USC 371, of International PCT application, PCT/JP99/02181, filed February 3, 1999, and designating the United States which claims priority from United States provisional application Serial No. 60-074026, filed February 9, 1998.--

IN THE ABSTRACT

Please replace the Abstract with the new Abstract, attached on a separate sheet.

IN THE CLAIMS

Please amend claim 1 as follows:

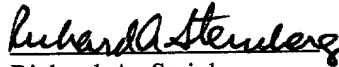
Claim 1, line 6, after "state" insert --under conditions--.

REMARKS

The specification is amended to update the sections on government sponsorship and related applications and to provide a new abstract. Claim 1 is amended for clarity.

Respectfully submitted,

by



Richard A. Steinberg
Attorney for Applicants
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--ABSTRACT OF THE DISCLOSURE

Amorphous, nanoporous silica gel having an open channel structure may be surface modified at higher loading of surface modifying ligands, e.g., 7.5 mmole per gram, than known nanoporous silica gels. In one embodiment, an amorphous silica gel has a bimodal pore size distribution of pores at about 10 nanometers and at about 10 microns, and a bulk density of about 0.2 to about 0.25 g/ml. Surface modification with functionalized ligand groups, effective for selective adsorption or reaction catalysis, is achieved by gelling silica sol solution to form a wet silica gel, maintaining the gel at a relatively low elevated temperature in a moist state to obtain a wet nanoporous silica gel having a plurality of open channels within the gel structure and silanol groups on the surface and reacting the surface silanol groups with the ligand group to introduce the functionalized group. The surface modifying reaction may be carried out concurrently with the gelling of a silica precursor in an aqueous alcoholic medium. 3-mercaptopropyltrialkoxysilane is an exemplary ligand introducing compound. The chemically surface modified silica gel may be used, for example, to remove or concentrate metallic substances in a liquid, or to separate two or more metallic impurities from a mixture thereof, or for cleanup of oil or chemical contaminants from the surface of a body of water.--

ION SEPARATION USING A SURFACE-TREATED XEROGEL

For purpose of the United States Designated Office, this invention was funded in part by a government grant from the Small Business Administration and the U.S. government retains certain rights to this invention.

This application claims priority from United States provisional application

- 5 Serial No. 60-074026, filed February 9, 1998, the entire disclosure of which is incorporated herein by reference thereto.

Technology Background and Comparison with existing Art:

- The most efficient way of removing metal ions from a solution is to first adsorb the ions onto the surface of a solid and then remove or regenerate the solid after it is
- 10 fully loaded with the target ions. Such a method can be applied to water purification in a continuous operation with water flowing through a column or over a fixed bed of the solid adsorbent. Commercial ion-exchange resins are examples of this approach. Recent developments in this technical field include the incorporation of molecular recognition functional species (i.e. metal-binding ligands) onto the surface of various
- 15 inorganic or organic carrier materials to achieve the selective adsorption of a particular group of ions from the background ions. Of all the carrier materials explored in this field of application, the synthetic silica gel is the most widely studied. This is because the synthetic nanoparticle silica contains a large amount of active silanol groups on the surface which is necessary for the incorporation of metal-binding
- 20 ligands and the required high surface area necessary for achieving rapid high-capacity adsorption.

Although much prior art has been developed based on the principle of incorporating metal-ion binding functional groups onto the surface of nanopore silica, the characteristics of the resulting silica-ligand composite products may differ significantly^{1,2,3,4,5,6,7} depending on the routes of processing. Different processing

5 techniques may start with silica gels similar in porosity and specific surface area (surface area per gram of silica) but could end up with products of distinctly different loading of the ligand groups. Or, two composites may contain a similar amount of loading of functional groups and yet differ considerably in adsorption efficiency. For the chemical modification of high surface area silica such disparities exist primarily
10 due to the effects of high interfacial stresses as well as the condensation reaction of surface silanol groups under the enormous stresses. The stress produced by the interfacial tension on the solid matrix is quite high. From the following conjecture, we know the capillary stress is inversely proportional to the pore size. For nanometer size pores the stress can be in the range of 100 Mpa.

15 Pore Dimension $\approx r$, Surface Tension = σ

$$\text{Stress} = \frac{\text{Force}}{\text{Surface Area}}$$

$$\text{Stress} \approx \frac{\sigma r}{r^2} \approx \frac{\sigma}{r}$$

20 Structure collapse may occur due to excessive capillary stress and the condensation among silanol groups at the surface. The shrinkage and the subsequent condensation reaction not only reduce the surface area, but also close off many channels, reducing access of the inner surface to the diffusion of large molecules.

The morphological details of the silica-ligand composite dictate the adsorption efficiency of the composite adsorbent because a high adsorption efficiency would require the following:

- (i) a large number of pores,
- 5 (ii) a high loading of functional (ligand) groups on the pore surface,
- (iii) many open channels connecting those pores; allowing an easy access for target ions to reach and bind the ligands on the pore surfaces.

To maintain open pore-connecting channels while making a silica-ligand composite is the most critical and challenging task required for achieving high
10 performance in adsorption. Yet, normally, the openness of the interconnecting channels is not adequately characterized for a composite product because the degree of openness for a channel is relative to the size of the transporting species. The ultimate test of whether the channel is open enough or not in a silica-ligand composite is its performance during the test for adsorption efficiency.

15 A wet low-density silica gel normally contains a porous open-cell structure. Water flows and ions diffuse freely within this kind of open structure. Thus, the entire surface area of the pores can be accessed rapidly. The open porous structure will increase the efficiency and speed of ion adsorption in a water treatment operation. In addition, such an open structure is necessary for the incorporation of
20 large functional groups onto the entire surface. Without an open structure, the incorporation of the functional groups in the preparation of the silica-ligand composite and the binding of targeted ions onto those ligands in a treatment operation become extremely slow and inefficient. The prior art includes many attempts to graft various ligand groups onto the surface of porous silica for ion-

specific adsorption. However, because of the inefficiency, the loading and adsorption capacities of those ligands were consistently lower than 1 mmole per gram of silica^{8,9,10,11,12,13,14,15,16}.

During drying of a gel, capillary stresses resulting from the surface tension of the meniscus in the pore can shrink and crack the nanopore material. The shrinkage becomes irreversible when crosslinking occurs with the condensation reaction of the surface silanol groups. Known treatments to reduce shrinkage include lowering the interfacial tension and minimizing the condensation reaction occurring among the surface silanol groups. Gel shrinkage leads to channel narrowing and ought to be prevented whenever possible. One approach to preserving an open structure is to support the pore structure against shrinkage with micelles formed by surfactant molecules. The surfactant molecules also lower the surface stress effectively, reducing the driving forces of shrinkage and surface condensation reactions.

Recently, scientists at DOE Pacific Northwest Laboratory¹⁷(PNNL) and Michigan State University¹ synthesized mesoporous silica (MS) materials containing functionalized organic monolayers that are very efficient in removing mercury from waste streams. The mesoporous silica material was prepared by mixing inorganic precursors in a solution containing surfactant micelles. The surfactants formed an ordered micelle structure. The precursors condensed around the regular structure forming a continuous silica phase. Subsequently, the surfactants were removed by thermal or chemical treatments leaving an ordered nanopore structure. See also, for example, U.S. Patent Nos. 5,622,684, 5,834,391, 4,981,825, 5,114,691, 5,672,556, 5,712,402, 5,726,113, 5,785,946, 5,795,559, 5,800,799, 5,800,800, 5,840,264, 5,853,886, the disclosures of which are incorporated herein in their entirety by reference thereto.

The synthesis of a family of mesoporous molecular sieves (M41S)¹⁸¹⁹ as described above was first reported in 1992 by scientists at Mobil R&D (see also, for example, U.S. 5,145,816, U.S. 5,220,101, U.S. 5,378,440), the disclosures of which are incorporated herein in their entireties by reference thereto. They used cationic surfactants to assemble silicate anions from solution. The micellar assemblies of quaternary ammonium cations (cationic surfactant S⁺) are the structure-directing agents. The surfactants formed an ordered micelle structure. Their strong electrostatic interactions with anionic silicate oligomers led to condensation of inorganic precursors around the regular structure forming a continuous silica phase.

There are three different members in the M41S family of materials: MCM-41 (hexagonal), MCM-48 (cubic), and MCM-50 (laminar). Since then, several other synthesis routes, involving different variations of charge matching and electrostatic interactions, were developed. The differences in pathways can be represented by the following combination of charge assemblies²⁰: (a). S⁺I⁻, (b) S⁻I⁺, (c) S⁺X⁻I⁻, (d) S⁻M⁺I⁰, and (e) S⁰I⁰ (product is called HMS), where, S: Surfactants, I: Inorganic Precursors, X: Halides (Cl⁻ or Br⁻), M: Metal ions (Na⁺, K⁺).

Removal of surfactants from the composites leads to mesoporous silica. The surfactants can be removed either by calcination or solvent extraction. Following the hydration of mesoporous silica surface (increasing surface silanol Si-OH population) the pore surface is incorporated with mercaptopropyltrimethoxysilane. Incorporation of ligands on the mesoporous silica developed by such a practice is much more effective than similar reaction with ordinary dry silica gel because of the increased access through the designed open channels in the former¹. Technology developed at PNNL demonstrated that using mesoporous silica with a chemically modified surface

as an adsorbent elevated the efficiency of ion removal to a high level. The new material, called functionalized monolayers on mesoporous support (FMMS), has a distribution coefficient (metal weight percent in silica/metal ion weight percent in solution) as high as 340,000. The residual ion concentration after treatment is at the
5 ppb (parts per billion) level.

While there have been significant advances in the art of mesoporous adsorbent technology still further improvements in performance and simplification of production would be highly desirable.

Summary of Invention

10 The present invention, in one aspect thereof, provides an improved surface modified silica and a method for producing same, characterized by chemically modifying a freshly produced (i.e. gelled without prolonged aging) silica gel still in its wet state with molecular recognition ligand groups. This new class of silica-ligand composite, referred to herein as, Chemically Surface Modified Gel (CSMG), has a
15 characteristic open pore structure as well as an exceptional high loading of surface ligands, both resulting from controlling the interfacial energy and processing kinetics during its preparation. Compared with existing art in the field, including the functionalized mesoporous silica mentioned above, products of this invention differ in at least the following categories:

20 (1) composition: much higher loading of ligands (e.g., 7.5 mmole per gram of support),

(2) morphology: open channels connecting nanopores; in preferred embodiment open channels connect micro- and nanopores,

- (3) adsorption efficiency: majority of the loaded ligands are accessible,
- (4) processing efficiency: significantly reduced processing time,
- (5) solvent systems of processing: environmentally benign solvents,
- (6) structure: amorphous, non-crystalline.

5 According to the calculation method reported in the literature (17), the surface density of fully dense monolayer coverage, as indicated by solid state NMR studies, was estimated to be 5×10^{18} molecules per square meter of surface area. Following the author's method of calculation, the ligand loading percentage on the silica surface achieved with the present invention is close to 100%. (Calculation is based on the

10 loading of 7.5 mmole ligand per gram of silica, which was determined by the electron energy-dispersive spectroscopy (EDS) data shown later in the section of characterization data, for a specific surface area of $900 \text{ m}^2/\text{g}$ silica.) In addition, the utilization of the surface ligands of the CSMG derived by this invention for binding metal ions is far more efficient (rapid and complete) than the range observed with the

15 existing art. (Adsorption tests done by mixing adsorbent with waste solution for one hour indicated that the utilization of the surface ligand group is $> 50\%$ for this invention versus $\leq 25\%$ for existing art). Although not intending to be bound by any theory of operation, it is believed that in the CSMG of this invention, the dense ligand groups are randomly distributed on the convex particle surfaces, therefore

20 spread outwardly and are more accessible for binding metal ions from the solution.

The following table provides a direct comparison of the CSMG of this invention with existing art:

	Range observed for existing art	This invention (CSMG)
Ligand loading	0.1 ~ 5 mmole/g silica	~7.5 mmole/g silica
Adsorption Efficiency	0.1 ~ 2.5 mmole metal/g silica	3 ~ 7.5 mmole metal/g silica
Morphology (Pore size distribution)	One type, 2 ~ 15 nanometer	Bimodal (10 nanometer and 10 micron)*
Reaction Time for attaching ligands	12 ~ 48 hours	1 ~ 2 hours
Solvent systems for thiol ligand incorporation	Chloroform, toluene, benzene	Water and ethanol**

* One scale (~10 nanometer) of pores are generated naturally with the silica gelation

10 process, these are referred to in some literature as "mesopores"; additional open pores of micron sizes are artificially created with the addition of an insoluble liquid plus an appropriate surfactant to control the pore size. Some prior art, see, e.g., U.S.

5,622,684, in addition to mesopores include textural mesopores, however, these are

only 1 to 2 order of magnitude larger than the framework-defined mesopores. In the
15 present invention, the CSMG has a porosity of approximately 90% by volume and less than about 10% of the total pore volume is provided by the micropores.

**The solvents combination for processing is specific to the choice of the ligand group; other combinations, e.g., water + methanol and water + tetrahydrofuran (THF), may be used depending on the molecular composition of the ligand group.

20 The present invention, in another aspect thereof, also relates to the chemically surface modified silica gel (CSMG) produced by the process of this invention. In still another aspect, the invention is directed to the use of the CSMG for removing metallic or non-metallic (e.g., organic) impurities from a liquid containing such metallic or non-metallic impurities. The invention also provides a method of forming
25 a nanoporous wet open-cell silica gel precursor for the CSMG.

Thus, the present invention provides a process for the preparation of a new class of material, Chemically Surface Modified Gel (CSMG), suitable for the removal of heavy metal waste arising from aqueous streams such as those generated from decontamination and decommissioning operations, as well as for removing organic waste, such as large oil spills or chemical spills. Metal ions of interest that are covered by the Resources Conservation and Recovery Act (RCRA) include mercury (Hg^{2+}), silver (Ag^+), lead (Pb^{2+}), cadmium (Cd^{2+}), and copper (Cu^{2+}). Some waste treatment facilities, such as, the DOE Weapons Complex, are subject to requirements that mandate very low levels for some metals in effluents (e.g. 0.004 mg/L silver) (U.S. Department of Energy, mixed Waste Focus Area, Technical Baseline Results, 1996). This requires technologies beyond commercially available ion exchange and specialty adsorbent systems. The present invention enables synthesis of CSMG with mercaptan functional groups attached to the surface. This material exhibits exceptionally high efficiency in adsorbing mercury ions. It is believed that the high efficiency is due to three factors: large surface area, high loading of mercaptan groups, and the low solubility product constant of HgS ($K_{sp} = 1.6 \times 10^{-52}$). Because of the low K_{sp} 's of Ag_2S , PbS , CdS , CuS (6.69×10^{-50} , 9.05×10^{-29} , 1.40×10^{-29} , 1.27×10^{-36} respectively), this CSMG is as effective in adsorbing Ag^+ , Pb^{2+} , Cd^{2+} , and Cu^{2+} as it is in adsorbing Hg^{2+} .

The present invention further provides a process which optimizes the attachment of molecular recognition ligand groups onto the surface of very high surface area and high porosity silica gels. In this process, the value of solubility product constants (K_{sp}) is used as guidance regarding the choices of effective functional groups. These CSMG materials can be made commercially viable based on

the extremely low cost and easy processing of the substrate materials used. This will allow very efficient separation of toxic heavy metals from waste streams at cost effective rates. These adsorbents will also be useful for high-value applications in many other fields, including reaction catalysis, wherein, as well known in the art, the functionalized ligand groups have catalytic activity or adsorb metal ions which exhibit catalytic activity, as well as addressing specific industry needs, such as, for example, DOE Weapons Complex waste treatment facilities.

Thus, the process for producing a chemically surface modified silica gel according to this invention includes the following steps of:

- 10 (a) gelling a silica sol solution to form a wet silica gel;
- (b) maintaining the silica gel at a temperature in the range of from about 40 to about 80°C in a moist state to obtain a wet nanoporous silica gel having a popularity of open channels within the gel structure and silanol (Si-OH) groups on the surface thereof; and
- 15 (c) reacting with the silica precursor during gelling (one-phase process) or with the wet nanoporous silica gel after gelling (two-phase process) with, for example, a mercaptoalkyltrialkoxysilane, or other molecular recognition functional ligand group, to introduce a functionalized group effective for selective adsorption and/or reaction catalysis, preferably in an aqueous alcoholic medium under an inert atmosphere and
- 20 at an elevated temperature within the range of from about 40°C to about 80°C to cause the functional ligand group e.g., mercaptoalkyltrialkoxysilane, to condense and react with the surface silanol groups to thereby obtain a chemically surface modified silica gel; and

(d) as necessary, drying the chemically surface modified silica gel.

The unique features of the CSMG derived from this invention are attributed to several novel processing practices employed in this invention, as described below. The incorporation of ligand groups is integrated with the preparation of the silica gel.

- 5 According to one embodiment of the invention, the reaction of the ligand groups with the silanol groups in the silica occurs during the gelation reaction (one-phase process). In an alternative embodiment, the reaction of the ligand groups is carried out with the fresh (i.e. without substantial aging after gelling) wet silica gel after the gelation reaction (two-phase process). For both of these embodiments, using a wet
- 10 gel, the solvent in the pores prevents shrinkage against surface stress and preserves the porosity and the open structure during processing. Moreover, a mixture of water and a ligand specific co-solvent is used as the solvent system during the gelation and the incorporation of the ligand. In the example given below, ethanol, a low liquid, is used as co-solvent with the incorporation of mercaptopropyltrimethoxysilane. Using a
- 15 low surface tension co-solvent such as ethanol reduces the interfacial energy of the modified silica particles considerably and, therefore, assists in the prevention or reduction of cell collapse.

The preservation of an open channel structure, as well as the reduction in interfacial energy by the co-solvent, not only improve the adsorption characteristics of

20 the CSMG product but also considerably simplifies the processing procedures. The open channels and the reduced surface energy allow rapid diffusion of the ligand molecules. The rapid diffusion is further accelerated by the incorporation of micropores as previously described. Additionally, the processing of CSMG in this invention does not require pretreatment of the silica surface. The fresh wet gel

contains many surface silanol groups which are strongly reactive to the ligand species. Contrary to a freshly prepared wet gel, an aged and dried silica gel does not have enough active silanol groups due to prolonged dehydration. The integration of ligand incorporation with the preparation of wet silica gel in this invention eliminates the

5 lengthy drying (dehydration) and re-hydrolyzing (hydration) procedures which are inherent to other processes in existing art. The comparison of the CSMG (two-phase) process with the processes of making mesoporous silica-ligand composite in the following table illustrates this point clearly.

Supporting Silica Substrate		MCM-41 by S^+T^-	MCM-41 by S^+XT^+	HMS by S^+T^-	Invention Sol-Gel
Preparation of Nanopore silica	Starting materials	Silica precursors $C_nH_{2n+1}N(CH_3)_3Br$	TEOS $C_nH_{2n+1}N(CH_3)_3Br$	TEOS $C_nH_{2n+1}NH_2$	TEOS, Colloidal silica, or Na_2SiO_3
	Solvents	Water	Water	Water + Ethanol	Water + Ethanol
	Processing conditions	Autoclave at 100 °C for 6 days, or by aging it at ambient for 7 days	by stirring it at ambient for 7 days	by aging it at ambient for 18 hours	Stirring at 60 °C for 2 hours; aged at 60 °C briefly
	Calcination Or Solvent extraction	630°C for 4 h (heating rate 2 °C/min) Hot (45°C) EtOH for 1 hour, Filtered and washed with ethanol repeated Air dried in an oven at 80 °C for 1 hour	(the last one in boiling EtOH)		No need
Surface Modification		PNNL Technology		MSU Technology	Invention CSMG
Incorporation of mercapto-propyltrimethyl silane	Hydration of silica	Reflux with deionized water for 3-4 hours		HMS dried under vacuum at 100 °C	Wet silica gel with MPTMS in ethanol
	Condensation	Reflux with MPTMS in toluene for 4 hours May require overnight stirring and drying		Reflux with MPTMS in toluene for 48 hours	aqueous solution stirred under nitrogen at 60 °C for 2 hours
	Solvents	chloroform, toluene, benzene (for different approach and loading capacities)		Toluene	Water + Ethanol

Brief Description of the Drawings

Figure 1 is an EDS spectrum of silver-laden adsorbent according to the invention.

Figure 2 is an IR spectra of (A) silica gel, (B) mercapto-functionalized silica gel, and (C) mercapto-functionalized adsorbent after silver (Ag^+) adsorption, all according to this invention.

Figures 3, 4, 5 and 6 are SEM photographs at magnifications of 556X, 1112X, 2225X and 4450X, of a silica gel having bimodal pore size distribution according to the invention.

10 Detailed Description of the Invention

In the present invention, a silica gel is prepared from a precursor solution derived from tetraethoxyorthosilicate (TEOS), or colloidal silica (for example, Ludox), or ion-exchanged sodium silicates, and the incorporation of a surface monolayer of functionalized ligand groups is integrated with the preparation of the silica gel (i.e. reacting during the gelation or immediately following the gelation before gel aging), thereby making the CSMG according to this invention. In order to have a compatible medium for incorporating the monolayer and a low interfacial tension for reducing the shrinkage of the gel, a specific solvent system may be chosen according to the composition of the ligand functional group. The choice of the functional group and the processing conditions of CSMG, including the solvent system, will dictate the adsorption efficiency of the final products. High adsorption efficiency may be achieved by (i) chemiadsorption of targeted ions on the surface; (ii) large surface area; (iii) open porous structure, and each of these factors is described in further detail.

(i) *Chemisorption of targeted ions on the surface*

The chemical properties of a gel surface are modified so that the target ions form chemical rather than physical bonds onto the surface. The modification with a ligand functional group increases the bonding energy of the metal ion to the silica surface sites. Increasing the bond energy will exponentially decrease the residual concentration of the ion in the solution at equilibrium. For example, at room temperature, reducing residual ion concentration from ppm (parts per million) to ppb (parts per billion) would require an increase of ca. 17 kJ in bonding energy. By chemically modifying the gel surface with a selected functional group the difference in energies of bonding the metal ion with the gel surface and solvating the metal ion in water could be effectively increased. This increase in bonding energy will result in a significant reduction in the residual concentration (ca. 6 kJ for a change of one order of magnitude in residual concentration) of the metal ion at adsorption equilibrium. The data of ion-ligand solubility product constant (K_{sp}) may be used as a direct reference for selecting appropriate functional groups to control the residual ion concentration.

(ii) *Large surface area*

The accessible surface area of a low-density CSMG is very large. Because the silica particles are of nanometer size, the surface area of a low-density gel is in the range of from about 800 to about 1000 m²/g. It is two orders of magnitude higher than the surface area of ordinary ion-exchange adsorbent with a particle size of 1 micron or larger. This increase in surface area will result in a proportional increase in reaction speed of any interfacial reaction. Additionally, once loaded with functional groups, a large surface area leads to a greater adsorption capacity. Experimental

results, as described below, clearly demonstrate this outstanding advantage of the surface modified nanogel. The present invention controls the gelation process to create the ideal gel morphology, i.e. a large surface area with many reactive silanol (Si-OH) groups (for the incorporation of surface functional groups). In particular, following the gelation reaction aging is limited to only a very brief duration, usually from about 30 to about 60 minutes, sufficient to allow secondary bond formation but too short for any significant degree of cross-linking or other pore collapsing reactions to occur.

In a gelation reaction, the backbone of the structure (long chain bonds) is formed rapidly at first, increasing the viscosity and slowing down additional bond formation. Aging after a gelation reaction allows cross-linking (forming local ring-closing bonds). Forming a small ring structure enhances the mechanical strength of the gel, but also closes off some open channels. Both high mechanical strength and channel openness are generally required in field applications. In the present invention, therefore, the processing conditions are controlled in order to achieve an optimized morphology: a strong but open gel structure.

(iii) Open porous structure

In order to incorporate functional groups on the surface of a low-density silica gel while it is in a wet state, it is necessary to control the gel morphology and to minimize the surface tension of the solvent system in order to preserve the high surface area and maintain a large number of open channels. Replacing water with a solvent of low surface tension reduces the shrinkage. Literature reports²¹ also indicate that reacting surface silanol groups with organic molecules before drying could preserve the open pore structure. In the present wet gel process, the pores are

filled with incompressible liquid, which provides support against capillary stress.

Incorporation of HS-CH₂-CH₂-CH₂-Si(OMe)₃ (MPTMS) onto the surface of a wet silica gel is achieved by using a mixture of solvents (water and ethanol) to lower the surface tension.

5 Additional open pores of micron sizes are created with the addition of an insoluble liquid plus an appropriate surfactant to control the pore size. These artificially created channels are intended for connecting the domains of nanopore silica in order to further facilitate the adsorption speed and efficiency.

Characterization of the Composite and Adsorption Capacities

10 The CSMG adsorbent material of this invention is essentially a tightly packed fractal-like arrangement of primary particles of approximately 10 nanometers particle size. The bulk density of the composite made by this invention is in the range of about 0.2 to 0.25 g/ml (determined with a Quantachrome mercury porosimeter). The specific surface area of the silica before the incorporation of the ligand groups is in
15 the range of about 600 to 1100 m²/g. The skeletal density of the silica was measured with a helium pycnometer (Micromeritics, Pycnometer AccuPyc 1330). The specific surface area was characterized by gas adsorption (Micromeritics, Gemini Surface Area Analyzer). Other properties were calculated according to the following set of equations:

20 Pore Volume = $\left(\frac{1}{\text{bulk density}} \right) - \left(\frac{1}{\text{skeletal density}} \right)$

Pore Size = $\frac{2 \times \text{surface area}}{\text{pore volume}}$

25 Porosity = $\left(1 - \frac{\text{bulk density}}{\text{skeletal density}} \right) \times 100\%$

Differences exist due to different degrees of gel shrinkage during drying before characterization.

At the completion of the surface reaction, the CSMG is washed several times with water, replacing the solvent mixture. Two types of characterizations may be performed. First it is confirmed that the MPTMS has successfully formed a monolayer on the silica surface. This is done through NMR, IR, and EDS spectra. Compositional analysis indicates that the relative concentration of sulfur on the CSMG surface is correlated to both the ratio of MPTMS to silica and the reaction time. As expected, higher ratios of MPTMS to silica and longer reaction times result in more thiol groups on the surface. This in turn, yields improved heavy metal adsorption. Verification of bonding can be seen in the accompanying Figures 1 and 2.

EDS and IR spectrometric analysis were also performed on a representative silver laden sample. The EDS spectrum (Figure 1) clearly indicates the presence of both sulfur and silver. The IR spectra of three forms of silica gel are shown in Figure 2. The top curve (A), is for untreated silica gel. Strong adsorption bands at 1089 cm^{-1} and 3430 cm^{-1} are attributed respectively to the stretching vibrations of Si-O-Si, and O-H on the surface. This should be compared to curve B, the spectrum for functionalized adsorbent. Here, bands at 2924 cm^{-1} , 2565 cm^{-1} , 1454 cm^{-1} , and 688 cm^{-1} correspond to CH_2 , SH, CH_2S , and $-(\text{CH}_2)_3-$, respectively, and show that MPTMS bonded to the surface of the silica. Finally, after silver ion adsorption (curve C), the band at 2565 cm^{-1} disappears and one at 1384 cm^{-1} results from the newly formed Ag-S bond. This clearly demonstrates that silver ions have bonded to thiol groups on the surface of the adsorbent.

Because 100% surface coverage of ligand can be obtained with the methods disclosed, this invention allows a complete range (from 0 to 100%) of surface coverage with the ligand groups through the control of reaction stoichiometry and kinetics. Partial coverage may be obtained with either a reduced degree of reaction (low reaction yield) or a lowered starting concentration for the ligand (longer processing time). The practical lower bound of the surface coverage by this invention for each kind of ligand group may be determined by the cost-effectiveness of producing the product under the constraints of the low reaction yield or the long processing time.

A second type of characterization allows for the determination of the efficiency as well as the capacity for metal ion adsorption by the CSMG. Atomic adsorption spectroscopy may be used to evaluate the concentration of metal ions before and after treatment with CSMG.

The efficiency of purification is characterized by the partition coefficient of metal ions distributed between the CSMG and the solution at equilibrium (i.e. weight % of ion in the CSMG divided by the residual weight % of ion in solution). The partition coefficient remains a constant at low adsorption concentration, equivalent to an equilibrium constant. At moderate to high adsorption, the coefficient is a function of adsorption concentration and ought to be characterized for a range of concentrations.

The following method may be used to evaluate the adsorption efficiency of the CSMG according to this invention.

To test the ability of adsorbent for purification of metal-contaminated water, a batch adsorption experiment at room temperature was performed. 10 mg of the adsorbent produced as in the following Example 2 was stirred with 50 ml of metal ion solution for 30 minute at initial concentration ranging from 5 to 10 ppm. Metal ion concentrations before (C_{initial}) and after (C_{eq}) treatment were determined by atomic adsorption spectroscopy. Results are shown in the following table.

	C_{initial} (ppm)	C_{eq} (ppm)	Adsorption mg/g at equilibrium	Partition coefficient mg per gram solid mg per gram solution
Ag^+	7.2	0.002	35.99	17,995,000
Pb^{2+}	6.5	0.028	32.36	1,155,714
Hg^{2+}	6.6	0.004	32.98	8,245,000
Cu^{2+}	6.6	0.012	32.94	2,745,000

The capacity of adsorbing metal ion by an adsorbent varies significantly with the pH value of the solution. For mercaptan loaded CSMG, the adsorption capacity is expected to rise with the increase of the solution pH. For CSMG of this invention the following tests are performed to determine the adsorption capacity of respective metal ions at pH value of three.

To test the maximum adsorption of adsorbent, 140 mg of the same adsorbent was mixed with 200 ml solution, adjusted to pH = 3, of respective metal ion for 1 hour at the initial concentrations indicated in the following table. Ion concentrations before (C_{initial}) and after (C_{final}) treatment were determined by atomic adsorption spectroscopy.

	C_{initial} (ppm)	C_{final} (ppm)	Adsorption (mg)	Capacity (mg/g adsorbent)
Ag^+	970	475	99	707
Pb^{2+}	1130	953	35.4	253
Hg^{2+}	904	388	103	737
Cu^{2+}	930	760	34	243

- 5 It is believed that this is the highest metal ion adsorption reported for silica based adsorbents.

Representative applications

Application 1. Waste water treatment

- Approximately 10,000 tons of mercury are discharged into water or ground
- 10 systems as industrial waste each year. Most removal operations require the separation of mercury ions from aqueous solution. Due to the high toxicity of the mercury ion, allowable concentration of the ion in the water after treatment is very low. Using the novel CSMG described herein would substantially lower the costs to reach the
- 15 required low concentration, relative to other adsorption methods. According to the present invention, on the other hand, a gallon of the CSMG can treat up to 30,000 gallons of wastewater, reducing mercury concentration from ppm to ppb. A test of adsorption capacity indicates that one gram (dry weight) of CSMG substrate according to this invention can adsorb 0.7 g of mercury under acidic condition. From
- 20 results of adsorption experiments and values of solubility product constants the inventive CSMG is also effective in treating wastewater containing silver (Ag^+), lead (Pb^{2+}), cadmium (Cd^{2+}), and copper (Cu^{2+}). All of these ions are major pollutants in various industries including those which manufacture batteries, computers, and photographic films. CSMG may be used for recovery use or waste clean up.

Application 2. Precious or rare elements extraction

Precious metals and trace elements normally exist in very low concentrations. One major cost of a traditional process is extraction of these precious metals and trace elements from a low-concentration stock solution. In many cases, the
5 preparation of high concentration and subsequent purification of the extract are the reasons for the high cost of these materials. CSMG may be used to extract low concentration (ppm level) metal ions selectively on to its surface. Due to its large surface area, CSMG can adsorb an amount almost equivalent to its own weight (see results of adsorption test). Thus, CSMG may be used to reduce the concentration
10 and purification cost of these materials significantly.

Application 3. Drinking water purification

In Asia and elsewhere, the rapid industrialization and population growth has endangered the supply and the quality of drinking water. As a result of ineffective pollution control and a significant increase in water consumption, cities now face a
15 crisis in supplying drinking water with acceptable quality. One proposed solution is to separate the water supply into two systems; one for drinking and another for other utility use. The CSMG of this invention may similarly be used for purifying water used to prepare bottled drinking water. The cost of bottled water in some areas is higher than the price of gasoline. CSMG may be used in the purification of drinking
20 water due to its high efficiency and loading capacity in ion adsorption.

Application 4. Solvent purification for electronic application

Processing of microelectronics has become one of the fastest growing and most profitable businesses worldwide. Due to the dramatic progress in device miniaturization, microelectronics products have the highest value per unit of material

used. Consequently, the microelectronics industry is capable of consuming many high technology and high-cost materials. One important requirement for solvent used in processing microelectronics is high purity. In particular, the ion concentration in the solvent must meet very strict standards. At present, the standard for allowable residual ions is being pushed from the sub-ppm level to the ppb level. Thus, in the extreme case of semiconductor processing, the solvents may require an on-site purification to remove contaminants occurring during its shipment. Reducing the ion level in a solvent from ppm to ppb is readily achievable due to the performance of CSMG with its comparable ease of processing.

10 Application 5. Preconcentration and Chromatography in Analytical Chemistry

CSMG adsorbent may be used for increasing the adsorption population of one specific ion or a group of ions. The large concentration difference for the specie in the CSMG adsorbent and in the solution presents application opportunities in analytical chemistry. Many analytical tests use only minute quantities of the sample.

- 15 When the concentration of the specie of interest is too low, the amount can not be detected. Using CSMG to preconcentrate the specie allows the accurate determination of the specie content even when only a small amount of sample is being analyzed. Moreover, the high adsorption capacity of CSMG makes it an ideal packing substrate for high efficiency liquid chromatography. A short CSMG column
20 may effectively separate ions with different partition coefficients.

The present invention thus provides a novel chemically modified silica gel substrate (CSMG) on the surface and pores of which there is incorporated a monolayer of ligand group (e.g., thiol). The starting silica material for forming a silica sol solution used to form a wet silica gel, may be, for example, an alkoxy silane,

especially tetraethoxy silane (TEOS), a colloidal silica precursor (e.g., Ludox), or a sodium silicate. The surface modification of the gel with, for example, mercaptopropyltrimethoxysilane, is done while it is still in a wet state (two-stage) or during the gelation reaction (one-stage). The adsorption efficiency of CSMG is more effective than the material made with mesoporous silicas. The invention CSMG is not only considerably more effective than adsorbents with similar composition, but in addition, may be produced with a much more efficient process. Using the process described above, the cost of producing the CSMG substrate is many times less than the cost of any other comparative substrate. The lower cost presents a significant advantage for any particular application (for example, wastewater treatment).

A silica gel made by a sol-gel process as described above normally contains tightly packed primary particles of size approximately 10 nanometers. As a result, the gel structure, packed from these primary particles, consists of open channels with a similar dimension (intra-particle channel size of approximately predominantly 10 nm). To facilitate and accelerate the diffusion of large species to and through these fine channels, a relatively small volume (e.g., about 10% of the total pore volume) of a second set of channels of micron size maybe artificially created during gelation to interconnect the finer (~10 nm) channels. An insoluble liquid (e.g., chloroform) and a surfactant (any anionic type, e.g., sulfate, sulfonate, soap, etc.) may be used to create such an interconnecting structure. The surfactant is used to minimize the interfacial energy between the insoluble solvent phases, and its amount should be far less than required for forming micelles (i.e. surfactant concentration sufficiently lower than critical micelle concentration to avoid micelle formation), as used in prior art templating processes.

As illustrated by the above application examples, the present invention provides liquid, e.g., waste water and aqueous or non-aqueous solvents, purification using CSMG as a super adsorbent for heavy metal ions. Using the process for producing CSMG according to this invention and the resulting CSMG product, it is possible to

5 achieve the following objectives:

- To increase the strength of CSMG material
- To control the structure-property relationship through processing parameters
- To optimize the reaction kinetics
- To improve the efficiency of processing
- 10 - To incorporate other selective functional groups onto the gel surface
- To develop techniques for recovering the adsorbed metal

These objectives are closely linked to the quality, cost, and processing, of the new CSMG product. Some of the properties and characteristics of the novel CSMG materials will now be described in further detail.

15 *1. Strength of CSMG material*

The porosity of the silica gel is very high (approximately 90 to 97%). The degree of cross-linking is very low. Channels among silica particles are numerous and open. These characteristics are responsible for the fast and extensive ion adsorption. However, the mechanical strength of CSMG may, for the same reasons, be too low
20 for some field applications. A weak and fragile substrate may be difficult to handle, especially for a large-scale industrial operation. Fine particles detached from a CSMG substrate could be a concern in an application, especially when they are loaded with toxic metal ions. Aging of the silica gel will increase the degree of cross-linking and improve the material strength. However, the degree of cross-linking must

be controlled, as described above, so as not to close off the pore channels. Increasing the density with the use of a more concentrated sol , as described below) will also effectively strengthen the gel structure. Since the gelation of such a concentrated sol system is much faster, the reaction kinetics must be adjusted accordingly.

- 5 The strength of the wet gel may be increased by, for example, taking into account the bulk modulus of the porous silica. The bulk modulus of a porous silica can be expressed by an equation²² $K = K_o(\rho/\rho_o)^n$, where (ρ is density, K_o is modulus at the reference density, and n is from about 3 to about 4). Increasing bulk density from 0.1 to about 0.25 will increase the modulus by a factor of approximately 15. Besides
- 10 density, the strength of a gel before and after drying depends on many kinetic factors such as aging, catalysis, reaction rate, etc. The kinetics of gel formation will determine the extent of the reaction and the initial microstructure of the gel, two important factors affecting K_o . Control of the kinetics of gelation to further increase K_o may also be accomplished.
- 15 Other techniques for increasing strength of the wet gel include using a concentrated sol solution and/or a layered silicate.

Concentrated sol solution

- So far, in all systems that have been used for making gels, TEOS, Colloidal Silica, and Sodium Silicate, the silica content of the starting solution was low. To increase
- 20 the final density, the silica content is increased to a desired level (e.g., >approximately 15%, e.g., about 20%) before gelation occurs, for example, by evaporating the solvent to increase the solids concentration. Solvent evaporation can be achieved either at an elevated temperature or a reduced pressure. The choice between these two conditions will be based on their effects on the kinetics of gelation

of a high-concentration sol. For example, to prevent premature gelation, a low-temperature (e.g., below room temperature) and/or reduced pressure, evaporation might be necessary.

Layered silicate

- 5 Increasing the solid content may also be accomplished by the addition of fine particle clays (layered silicates) into the starting solution. Layered silicates have been used to strengthen aerogels in the past, and may similarly be used to strengthen the CSMG of this invention. Clays of from about 20 to 30 micron particle size are preferred. According to earlier experiments, aerogels made with the addition of clay
- 10 greatly improves mechanical strength. Moreover, the plate geometry of a clay molecule provides a means for significantly altering physical properties in different directions with the control of the orientation of the plate molecules. Nanocomposites made of clay and polymers demonstrated exceptional improvement in thermal stability, thermal expansion coefficient, and reduced gas permeation. Adding layered
- 15 silicates to CSMG will prevent the loss of detached particles during an adsorption operation.

Surface modification and Cross-linker

- Surface modifications may also be used to improve gel strength. Since the surface functional groups of nanopore silica represent a large portion of the substrate,
- 20 modification of them leads to changes in bulk properties as well. In addition, the population of the ligand groups and the repulsion between them slows down the condensation of silanol groups. It is known that aerogels made with extensive surface methylation can withstand the capillary stress incurred during drying under ambient conditions⁶. The 3-mercaptopropyl-trimethoxy-silane molecules incorporated on the

surface have similar strengthening effects. As the loading of the surface monolayer is increased, mechanical strength of the CSMG improves as well. Other multi-functional oligomers (e.g., tri-[3-(trimethyloxysilyl)-propyl]isocyanurate) may be used to cross-link the CSMG for improving the strength. The size and stereochemistry of the oligomer molecules are screened so that incorporating them onto the CSMG surface will not block the diffusion of target metal ions.

2. Control of the structure-property relationship through processing

As noted above, a great deal of the cost of producing CSMG is in material processing. The properties, and therefore the performances, of the CSMG material are closely correlated to the processing conditions. In order to produce the most effective (performance/cost) CSMG, the structure-property and morphology-processing relationships of the CSMG material is determined. This may be accomplished, for example, by characterization of the particular surface modification processing condition utilizing, for example, TEM, NMR, and/or IR to determine the effectiveness of the surface modification scheme.

The processing conditions for gels made from TEOS, colloidal silica, and sodium silicates, must be monitored very carefully. It is the solvent which creates the porosity in these systems. High porosity material is mechanically weak. During drying, capillary stress, resulting from surface tension of the meniscus in the pore, may shrink and crack the material. For pores of nanometer size the stress can be in the range of a hundred pounds per square inch. In the wet gel process according to this invention, the pores are filled with liquid, which is incompressible. The capillary stress will cause very little shrinkage because of the low compressibility of the liquid. During drying, however, the liquid turns into vapor, which is highly compressible, and the stress

would tend to collapse the cells. Shrinkage resulting from cell collapse would reduce the porosity and may close off some open channels. Thus, the processing conditions of the gel may greatly affect the effectiveness of the subsequent surface modifications.

While much is known about the chemistry and kinetics involved in the gelation of plain silica sol, less detail is known about the variation of those parameters with the change in solvent content, silica density, temperature, and the pH. However, by controlling the kinetics of gelation using a solvent mixture with a low surface tension, a concentrated sol solution, and/or lower temperature, the reaction speed may be controlled so that the morphology and processing are optimized. Layered silicates may be used to strengthen the gels, as described above. However, care must be taken that these added ingredients do not alter the effectiveness of the modification reaction.

Using a series of controlled experiments and characterization work the effects of processing conditions on the overall adsorption efficiency of CSMG may be readily ascertained. Determination of the efficiency of adsorption in broader terms, including the extent of the adsorption, the speed of the adsorption, the effects of physical (for example, temperature) and chemical (for example, pH, other ionic species, etc.) environments on the adsorption and other interfering factors will then be known.

3. Optimization of reaction kinetics

One major advantage of a silica sol-gel system in processing is that the gelation kinetics can be easily controlled with the adjustment of the pH value. For an industrial product, a faster reaction usually allows a shorter processing time and a lower fixed (manufacturing) cost. Of course, the gelation must also be slowed down enough so that other processing procedures can catch up with the gelation. The

control of gelation kinetics is critical because the microstructure and the mechanical properties of a silica gel are dictated by it. Optimization of the reaction kinetics is further required due to the fact that the effectiveness of the surface modification is very sensitive to the properties and thus, the processing of the silica gel.

- 5 The reaction for loading ligand groups onto silica gel surfaces and subsequent treatments generally takes a couple of hours. The reaction rate, the reaction temperature, the pH, the initial gel morphology, are factors which may be controlled to optimize the rate of the surface modification reaction and/or to achieve a higher percentage of loading within a reasonable reaction time. A higher loading of
- 10 functional groups is effective to increase the adsorption efficiency and, in some cases, to improve the strength of the CSMG as well.

4. Efficiency of processing

- An industrial process, differing from a laboratory process, must deal with a very large quantity of materials. Consequently, many issues, which are negligible on a
- 15 laboratory scale, must be addressed properly during scaling up. For example, VOC (volatile organic compound), solvent recovery, fire hazards, waste treatments, scrap reuse are all important issues for industrial processing. Since CSMG is made from a low-density gel, the volume of solvent used for the reaction and washing is several times larger than the actual volume of the product. Even though relatively safe
- 20 ethanol may be used in place of benzene, the amount of solvent needed for processing may still present a problem in large scale production. However, those skilled in the art, will be able to design an efficient processing system so that all the processing issues mentioned above are satisfactorily addressed.

The conditions used in batch procedures may be adopted for a semi-continuous process. In particular, the reaction rates of each individual component are adjusted so that the flow of materials for the process are synchronized. In a continuous process the majority of the production may be carried out in an extruder. The
5 extruder may have many different zones, each one being designated for a different reaction.

5. Incorporation of other selective functional groups

Initial work incorporated the mercaptan functional group on the silica gel surface. Metal ions that normally precipitate with the sulfide ion (low solubility product, K_{sp})
10 are exhaustively adsorbed. By determining the solubility product value of different ion pairs other new surface modification schemes may be designed. K_{sp} and bonding energies may be utilized to choose the appropriate functional groups to be incorporated in the CSMG. As explained previously, solubility product constant (K_{sp}) is a direct indication of what type of functional group to choose for a specific ion.
15 Bonding energies of a precipitate or a complex ion may be used to estimate the effectiveness of adsorption. The free energy of the adsorption may be calculated and the partition coefficient, K_p (surface ion concentration/residual ion concentration), may be estimated, accordingly. Since in most cases, only very diluted solutions will be treated with the CSMG, the ideal solution scenario may be used to obtain the
20 entropy. For the species adsorbed on the surface, the entropy may be calculated by using a two-dimensional lattice model.

In qualitative analysis a group of ions can be selectively precipitated with one common ion; likewise, a functional group incorporated at the silica gel surface may selectively adsorb a group of counter ions as desired. Following traditional qualitative

analytical chemistry (of separating ions in solution) choices of additional functional groups for ion removal may be selected. Successful incorporation of new functional groups will extend the applications of CSMG as a product, and will also simplify the procedures of using CSMG for water or solvent purification. For instance, a multi-
5 zone column packed with CSMG of different functional groups may be used to achieve a complete purification with just one flow through the column.

Thus, as examples of representative suitable functional group providing ligands, mention may be made of, for example, mercaptans, such as, 3-mercapto-(mono- or di)-alkyl(di- or tri-)alkoxy silanes, e.g., 3-mercaptopropyltrimethoxysilane, 3-
10 mercaptopropyltriethoxy silane, 3-mercaptopropylmethyldimethoxy silane; amines, such as, 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, ethylenediamine mono-, di-, tri- or tetra-acetate, and the dithiocarbamate derivative thereof, N-[3-(trimethoxysilyl)propyl]ethylenediamine and the triacetic acid trisodium salt thereof; amides, such as chitin and chitin derivatives, e.g., chitosan; and the like. Other known
15 chelating agents, such as, for example, 1-nitroso-2-naphthol, 5-sulfodimethylisophthalate salts, e.g. Na, 8-quinolinol; and ion-exchange resins as well known in the art may also be used as the functional group providing ligands for the CSMG adsorbents of this invention. In this regard, mention is made of the literature references²³⁻³⁹, in the attached list of references, forming part of this application,
20 and which references are incorporated herein in their entireties by reference thereto.

6. Techniques for recovering metal from a waste stream

The high loading capacity of CSMG at saturation (about 0.7 gram Hg/gram CSMG) provides an opportunity for recovering the metals from CSMG after wastewater treatment. There are at least two options available for removing metal

ions from the surface of CSMG. One is to change the partition coefficient of the adsorbed metal ion by varying the temperature and/or the pH of the solution.

Regeneration of used CSMG material with recovery of adsorbed metal ions may be achieved using, for example, a concentrated HCl solution. This will significantly

5 increase the concentration of the metal ion in the solution and lead to a regeneration of the CSMG surface. The regenerated materials will retain high loading capacity and remain effective even after several cycles. Dissolving the CSMG in a hot basic solution will also result in a separation of the metal ion from the CSMG surface.

After being relieved from the CSMG surface, the metal ions can be reduced to metal
10 through chemical reaction or electrolysis. With a recovery option, the CSMG wastewater treatment bridges a complete cycle for the use of heavy metal materials.

The following experimental procedures are disclosed merely as examples of practicing this invention according to the detailed principles described above. Many variations in practices of this invention within the boundary of the working principles
15 and the scope of the claims may be recognized by those skilled in the art according to the principles and examples disclosed.

Example 1: Producing CSMG from TEOS by two-phase processing

Silica sol is prepared from TEOS, H₂O, ethanol and HCl, in the total molar ratio
1: 2: 4: 0.0007. The mixture of TEOS, H₂O, ethanol and HCl is stirred at 60 °C for 2
20 hours. A NH₄OH solution and variable amount of water is added to adjust the pH to 6 to 7 and to gel the mixture. Gelation normally occurs within a few minutes. The obtained wet silica gel is aged at 60 °C briefly (about 30 to 60 minutes) and washed with ethanol and water separately.

The mixture of 50g of wet silica gel and a variable amount (depending on the desired % of ligand loading) of 3-mercaptopropyltrimethoxysilane is added into a reaction vessel equipped with agitator, heating mantel, thermometer and nitrogen purge system. A solution of water and ethanol is used as the reaction medium. The amount of ethanol in this mixed solvent should be adjusted according to the amount of ligand desired in the mixture. The reaction mixture is heated to 50-60 °C for from 1 to 2 hours. After cooling down to room temperature, the product is filtered and washed thoroughly with ethanol and water successively.

Example 2: One-phase processing of CSMG

Silica sol is prepared from TEOS, H₂O, ethanol and HCl, in the total molar ratio 1: 2: 4: 0.0007. The mixture of 50ml of silica sol and a variable amount (depending on the desired % of ligand loading) of 3-mercaptopropyltrimethoxysilane is added into a reaction vessel equipped with agitator, heating mantel, thermometer and nitrogen purge system. Additional amount of water or ethanol is used to adjust the water/ethanol ratio in the solvent mixture so that their proportions are suitable for the amount of ligand desired. The reaction mixture is heated to 50-60 °C from 1 to 2 hours. Then, a NH₄OH solution is added to the mixture to induce gelation. After cooling the CSMG is filtered and washed thoroughly with ethanol and water successively.

Example 3: Incorporation of a ligand group different than thiol

Separately following the procedures of Example 1 and Example 2, 3-aminopropyltrimethoxysilane or chitosan are incorporated onto the surface of the silica gel with high loading, respectively, by the two-phase or one-phase embodiments.

Example 4: Creating micron-size interconnecting channels

Following procedures in Example 2 to create a one-phase mixture of ligand and silica sol, the reaction mixture is heated to from 50 to 60°C for from 1 to 2 hours.

After the mixture is cooled down to room temperature, 2 ml of chloroform and 0.2 to 0.5 gram of sodium dodecyl sulfate in water (2 to 5 ml) is added to the mixture. The mixture is heated to 30 to 40°C with vigorous stirring for 1 hour. Then, a NH_4OH (1N) solution is slowly added to the mixture until gelation occurs. After aging at 30 to 40°C, the product is filtered and washed thoroughly with ethanol and water successively.

10 *Example 5:*

Silica sol is prepared from 100g Nalcol 115 by adding 10 ml of 1M H_2SO_4 to adjust the pH to 6.78. The mixture gels within 30 minutes at room temperature.

A mixture of 50g of wet silica gel and a variable amount (depending on the desired % of ligand loading) of 3-mercaptopropyltrimethoxysilane is added into a reaction vessel equipped with agitator, heating mantel, thermometer and nitrogen purge system. A solution of water and ethanol is used as the reaction medium. The amount of ethanol in this mixture solvent is adjusted according to the amount of ligand desired in the mixture. The reaction mixture is heated to 50 to 60°C for from 1 to 2 hours. After cooling down to room temperature, the product is filtered and washed thoroughly with ethanol and water successively.

While the invention has been described above in connection with silica based CSMG and silica gel precursors, the invention is equally applicable to other metal oxide adsorbents, such as, for example, alumina, zirconia, titania, and the like, including mixtures of metal oxides. As well known in the art gels of the metal oxides
5 may be prepared similarly to the preferred silica gels, such as, for example, from the corresponding metal hydroxide precursors.

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WHAT IS CLAIMED IS:

1 Claim 1. A method of producing a nanoporous open-cell functionalized silica
2 gel having a plurality of open channels within the gel structure and silanol (Si-OH)
3 groups on the surface comprising

4 (a) gelling a silica sol solution to form a wet silica gel;

5 (b) maintaining the silica gel at a temperature in the range of from about 40 to
6 about 80 °C in a moist state to obtain a wet nanoporous silica gel having a plurality of
7 open channels within the gel structure and silanol (Si-OH) groups on the surface; and

8 (c) reacting a ligand group with the surface silanol groups to introduce a
9 functionalized group effective for selective adsorption or reaction catalysis.

1 Claim 2. A method for producing a chemically surface modified silica gel
2 comprising:

3 (a) gelling a silica sol solution to form a wet silica gel;

4 (b) maintaining the silica gel at a temperature in the range of from about 40 to
5 about 80°C in a moist state to obtain a wet nanoporous silica gel having a plurality of
6 open channels within the gel structure and silanol (Si-OH) groups on the surface
7 thereof; and

8 (c) reacting the wet nanoporous silica gel with a reactive ligand introducing
9 compound in an aqueous alcoholic medium under an inert atmosphere and at an
10 elevated temperature within the range of from about 40°C to about 80°C to cause the
11 ligand introducing compound to condense and react with said surface silanol groups
12 to thereby obtain said chemically surface modified silica gel; and

13 (d) optionally, drying the chemically surface modified silica gel.

1 Claim 3. A method for producing a chemically surface modified silica gel
2 comprising the steps of:

3 (a) reacting a silica precursor with a reactive ligand introducing compound in
4 an aqueous alcoholic medium under an inert atmosphere and at an elevated
5 temperature within the range of from about 40°C to about 80°C to cause the ligand
6 introducing compound to condense and react with said silanol groups before gelation
7 and subsequently adjusting the pH value of the solution to induce gelation, to thereby
8 obtain said chemically surface modified silica gel; and

9 (b) optionally, drying the chemically surface modified silica gel.

1 Claim 4. A chemically surface modified silica gel produced by the method of
2 claim 1.

1 Claim 5. A chemically surface modified silica gel produced by the method of
2 claim 2.

1 Claim 6. The chemically surface modified silica gel according to claim 5
2 wherein the ligand introducing compound is 3-mercaptopropyltrialkoxysilane.

1 Claim 7. A chemically surface modified silica gel produced by the method of
2 claim 3.

1 Claim 8. The chemically surface modified silica gel according to claim 7
2 wherein the ligand introducing compound is 3-mercaptopropyltrialkoxysilane.

1 Claim 9. A method of removing metallic impurities from a liquid which
2 comprises contacting the liquid with the chemically surface modified silica gel of any
3 one of claims 1-8.

4 Claim 10. A method of concentrating metallic content in a liquid which
5 comprises contacting the liquid with the chemically surface modified silica gel of any
6 one of claims 1-8.

7 Claim 11. A method of separating two or more metallic impurities from a
8 solution of the mixture of metallic impurities which comprises passing the solution
9 mixture through a column packed with the chemically surface modified silica gel of
10 any one of claims 1-8.

1 Claim 12. A method of recovering metal from a low-concentration feed
2 solution which comprises contacting the feed solution with the chemically surface
3 modified silica gel of any one of claims 1-8.

1 Claim 13. A method of producing a nanoporous open-cell silica gel having a
2 plurality of open channels within the gel structure and silanol (Si-OH) groups on the
3 surface comprising

4 (a) gelling a silica sol solution to form a wet silica gel; and

5 (b) maintaining the silica gel at a temperature in the range of from about 40 to
6 about 80°C in a moist state to obtain a wet nanoporous silica gel having a plurality of
7 open channels within the gel structure and silanol (Si-OH) groups on the surface.

1 Claim 14. A method for preparing a chemically surface modified silica gel
2 effective for adsorbing a target specie from a liquid containing said target specie
3 suspended or dissolved therein, said method comprising

4 (1) selecting a ligand molecule having a first functional group at one end
5 thereof reactive with the silanol groups of silica and a second functional group at an
6 opposed end thereof, said second functional group strongly binding to said target

7 specie, as determined by at least one of bond energy between the second functional
8 group and target specie or solubility product constant, K_{sp} ; and

9 (2) reacting wet silica gel with the selected ligand in a hydrophilic co-solvent.

1 Claim 15. A chemically surface modified silica gel produced by the method of
2 claim 14 which further comprises

3 (a) gelling a silica sol solution to form a wet silica gel;

4 (b) maintaining the silica gel at a temperature in the range of from about 40 to
5 about 80 °C in a moist state to obtain a wet nanoporous silica gel having a plurality of
6 open channels within the gel structure and silanol (Si-OH) groups on the surface
7 thereof; and

8 (c) reacting the wet nanoporous silica gel with a reactive ligand introducing
9 compound in an aqueous alcoholic medium under an inert atmosphere and at an
10 elevated temperature within the range of from about 40°C to about 80°C to cause the
11 ligand introducing compound to condense and react with said surface silanol groups
12 to thereby obtain said chemically surface modified silica gel.

1 Claim 16. A chemically surface modified silica gel produced by the method of
2 claim 14 which further comprises

3 reacting a silica precursor with said selected ligand molecule in said hydrophilic
4 co-solvent under an inert atmosphere and at an elevated temperature of from about
5 40°C to about 80°C to cause the selected ligand molecule to condense and react with
6 said silanol groups before gelation and subsequently adjusting the pH value of the
7 solution to induce gelation.

1 Claim 17. A method of separating a target specie from a ligand containing
2 said target specie which comprises contacting the liquid with the chemically surface
3 modified silica gel of claim 15 or claim 16.

1 Claim 18. A chemically surface modified silica gel according to claim 15 or
2 claim 16 wherein said second functional group strongly binds to an organic target
3 specie.

1 Claim 19. A method for removing oil or other organic chemical contaminant
2 spilled on the surface of a body of water, comprising contacting the contaminated
3 surface of said body of water with the chemically surface modified silica gel according
4 to claim 18 whereby the oil or other organic chemical contaminant at least
5 substantially adsorbed by said gel and thereafter removing the gel from the surface of
6 said body of water.

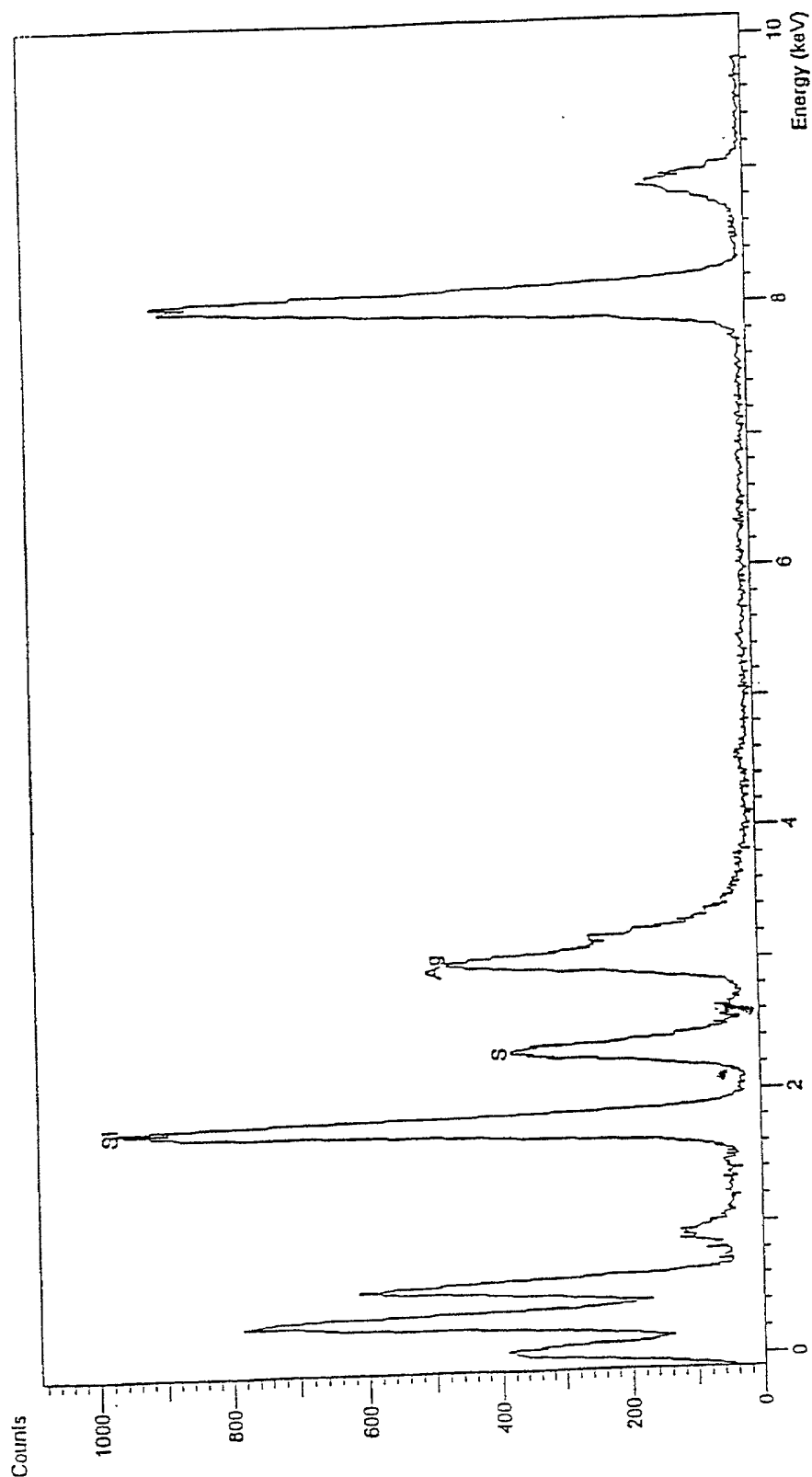
1 Claim 20. A chemically surface modified amorphous silica gel adsorbent
2 comprising

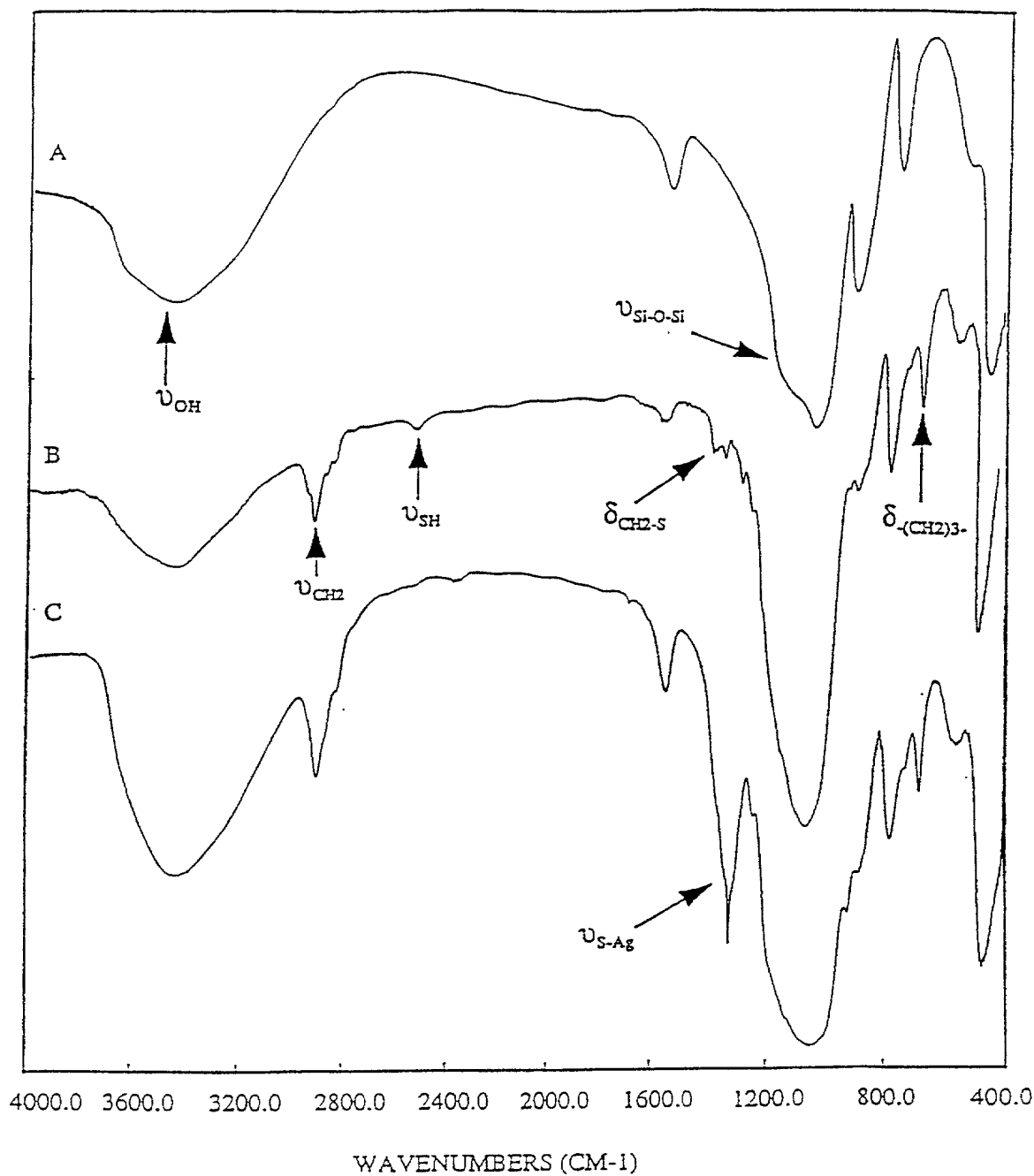
3 (i) bimodal pore size distribution of pores having pore diameters of about 10
4 nanometers and about 10 microns;

5 (ii) ligand loading of about 7.5 mmole ligand per gram silica gel; and

6 (iii) bulk density in the range of from about 0.2 to about 0.25 g/ml.

1 Claim 21. The silica gel adsorbent according to claim 18 wherein said ligand
2 comprises 3-mercaptopropyltrialkoxysilane.





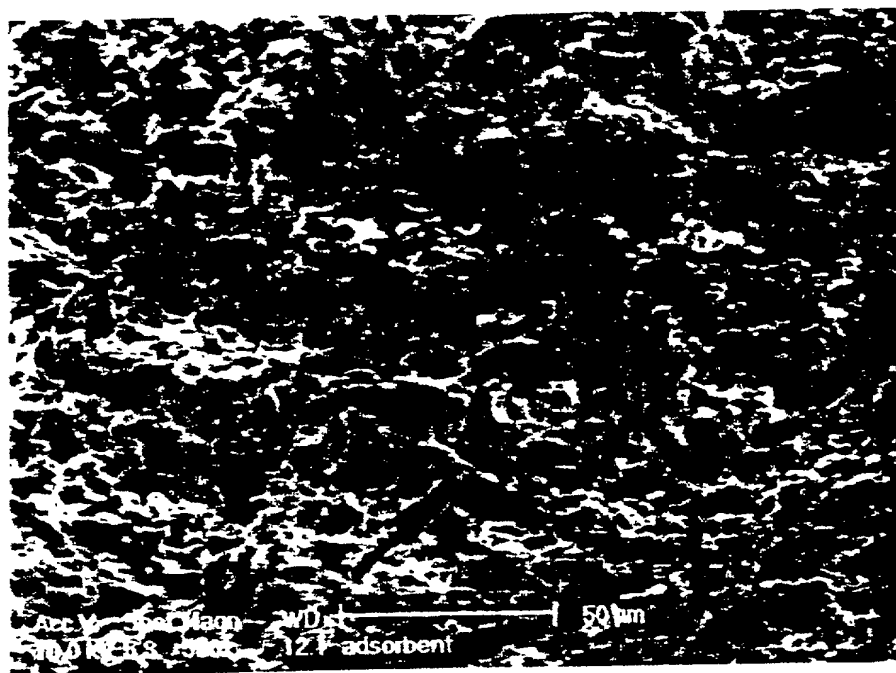


FIG. 3

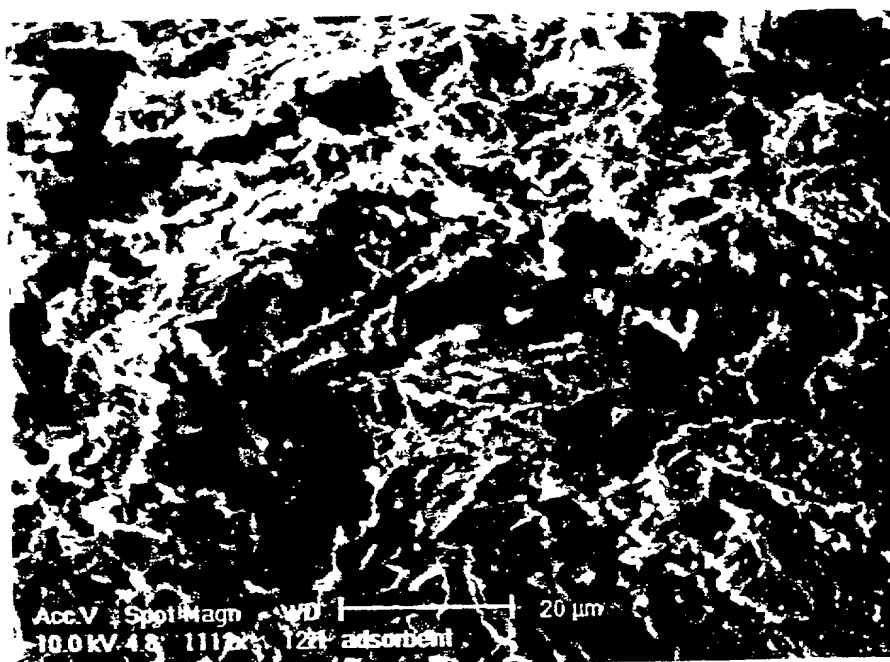


FIG. 4

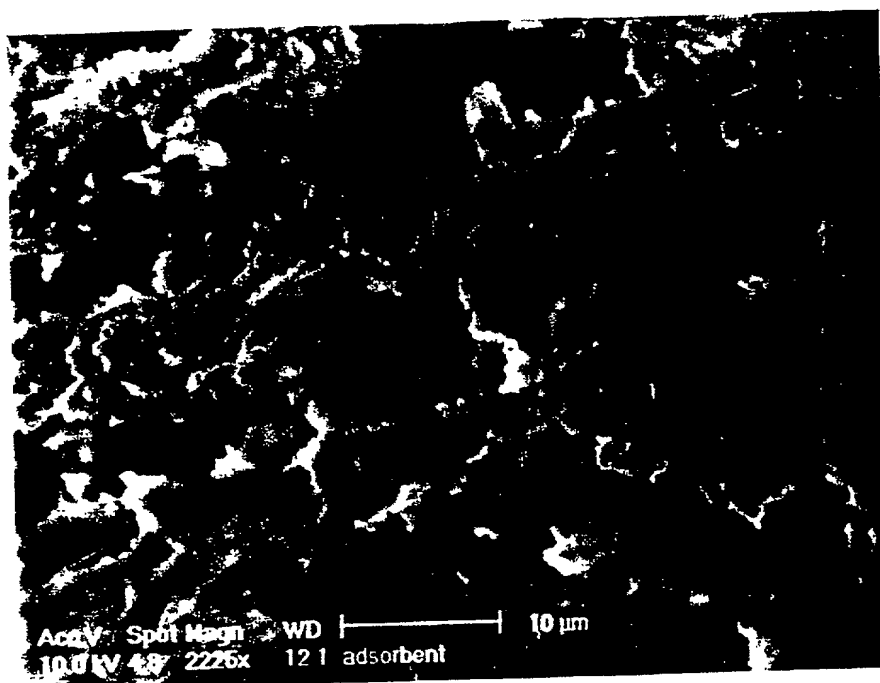


FIG. 5

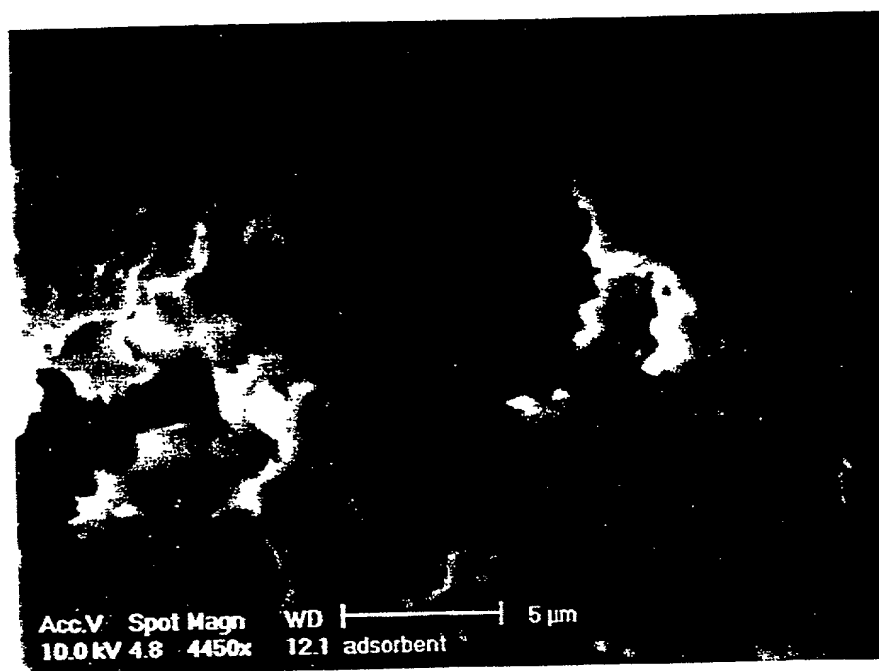


FIG. 6

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DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION (37CFR1.63)	Attorney Docket Number	ISTN-100	
	First Named Inventor	Arthur Jing-Min Yang	
	COMPLETE IF KNOWN		
	Application Number	/	
	Filing Date	Concurrently herewith	
	Group Art Unit		
<input checked="" type="checkbox"/> Declaration Submitted with Initial Filing	<input type="checkbox"/> Declaration Submitted after Initial Filing (surcharge (37CFR1.16(e)) required)	Examiner Name	

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

ION SEPARATION USING A SURFACE-TREATED XEROGEL

the specification of which (Title of the Invention)

☐ is attached hereto

OR

☒ was filed on (MM/DD/YYYY) **February 3, 1999** as United States Application Number or PCT International Application Number **PCT/US99/0218** and was amended on (MM/DD/YYYY) (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendments specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37CFR 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or 365(b) of any foreign application(s) for patent or invention certificate, or 365(a) of any PCT international application which designated at least one country other than the United States America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached?	
				YES	NO
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

☐ Additional foreign application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto.

I hereby claim the benefit under 35 U.S.C. 119(e) of any United States provisional application(s) listed below.

Application Number(s)	Filing Date (MM/DD/YYYY)	
60/074,026	February 9, 1998	<input type="checkbox"/> Additional provisional application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto.

[Page 1 of 2]

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eduty to disclose
prior application

U.S. Parent Application or PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (if applicable)

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Country	<u>United States</u>	Telephone	<u>703-549-2282</u>	Fax	<u>703-836-0106</u>

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Name of Sole or First Inventor:		<input type="checkbox"/> A petition has been filed for this unsigned inventor	
Given Name (first and middle if any)		Family Name or Surname	
<u>Arthur Jing-Min</u>		<u>YANG</u>	
Inventor's Signature	<u>X</u> <u>Arthur Jing-Min</u>	Date	<u>7-20-2000</u>
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		ZIP	
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